

SPECIFICATION

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[NO_x, Hg, AND SO₂ REMOVAL USING ALKALI HYDROXIDE]

Cross Reference to Related Applications

This is a continuation-in-part of U.S. serial number 09/683,267, filed December 6, 2001, pending.

Background of Invention

[0001] a. Field of the Invention.

[0002] This invention relates to methods and apparatuses for removing NO_x, Hg, and SO₂ from a gas stream.

[0003] b. Description of the Related Art.

[0004] Fossil fuels are burned in many industrial processes. Electric power producers, for example, burn large quantities of coal, oil, and natural gas. Sulfur dioxide ("SO₂"), nitrogen oxide ("NO"), and nitrogen dioxide ("NO₂") are some of the unwanted byproducts of burning any type of fossil fuel. Mercury ("Hg") is often also found in fossil fuels. These byproducts are known to have serious negative health effects on people, animals, and plants, and a great deal of research has been done to find a way to economically remove them from flue gas streams before they enter the atmosphere.

[0005] SO₂ is often removed from gas streams ("desulfurization") by scrubbing the gas with an aqueous ammonium sulfate solution containing ammonia. Examples of this process are disclosed in U.S. Patent Nos. 4,690,807, 5,362,458, 6,277,343, and 6,221,325, which are not admitted to be prior art by their mention in this Background section. The absorbed sulfur compounds react with ammonia to form ammonium

sulfite and ammonium bisulfite, which are then oxidized to form ammonium sulfate and ammonium bisulfate. The ammonium bisulfate is further ammoniated to form ammonium sulfate. The process does not remove NO or NO₂, however, which must then be dealt with using a different process.

[0006] NO and NO₂ (together known as "NOx") can be removed from a gas stream by contacting the gas stream with either ClO₂ or O₃ to convert NO into NO₂, and then scrubbing with an aqueous solution of a sulfur-containing reducing compound of alkali metals or ammonia, and a catalytic compound. Such a process is disclosed in U.S. Patent No. 4,029,739, by Senjo et al., which is not admitted to be prior art by its mention in this Background section. This process, however, does not remove SO₂, and requires the addition of chlorine or ozone into the system by some other means.

[0007] Some processes exist that remove both NOx and SO₂. In one such process disclosed in U.S. Patent No. 4,035,470, by Senjo et al., which is not admitted to being prior art by its mention in this Background section, NO is oxidized to NO₂ by contacting the gas with either ClO₂ or O₃ as above. Then the SO₂ is scrubbed with a sulfite and an oxidation retardant that suppresses oxidation of the sulfite to sulfate. Iron or copper compounds can also be added to depress oxidation. Optionally, ammonium hydroxide can be added to make sulfite and to react with CO₂ in the gas stream to make carbonate. Like in U.S. Patent No. 4,029,739 mentioned above, this process requires the addition of either chlorine or ozone, and further requires a consumable sulfite oxidation retardant. The referenced patent did not mention whether the byproducts included any valuable material like ammonium sulfate. However, both patents 4,029,739 and 4,035,470 require the addition of chlorine to a gas stream that is eventually released to the atmosphere, creating a serious safety concern.

[0008] Yet another process for removing NOx and SO₂ from a gas stream is disclosed in U.S. Patent No. 4,971,777, by Firnhaber et al., which is not admitted to be prior art by its inclusion in this Background section. In this process, NO is oxidized to NO₂ by the addition of organic compounds which decompose into radicals at high temperatures. Then an aqueous ammonia solution in which the pH is adjusted to be below 5.0 absorbs the NOx and SO₂. Firnhaber teaches the importance of holding the

scrubbing solution to a low pH, since higher pH levels produce aerosols of the ammonia salts that he says is an environmental burden to be thwarted. Ammonia aerosols are formed by gas phase reactions of ammonia vapor in the scrubber and create a blue haze or white vapor that emanates from the stack. This is also called "ammonia slip." Free ammonia in the atmosphere would be a serious health and environmental hazard. Firnhaber dismisses the possibility of aerosol removal means due to prohibitive investment costs and high pressure loss, for instance.

[0009] The typical method of removing mercury is to add activated carbon to the gas stream in order to absorb the mercury, and then mercury-containing activated carbon is collected in a bag house. This has the disadvantage of requiring an expensive particulate additive just to absorb one material, and a requiring bag house to collect the particles that were added.

[0010] What is needed, therefore, is a process that removes SO_2 , Hg, NO, and NO_2 from a gas stream that does not require addition to the gas stream of a catalyst, chlorine, ozone, or activated carbon, can occur at relatively high pH, and does not result in ammonia slip.

Summary of Invention

[0011] The present invention is directed to a process and apparatus that removes SO_2 , Hg, NO, and NO_2 from a gas stream that does not require the addition of a catalyst, chlorine, ozone, or activated carbon, occurs at a relatively high pH, and does not result in ammonia slip. A process that satisfies these needs comprises the steps of oxidizing NO to NO_2 and Hg to oxidized mercury, scrubbing SO_2 , NO, and NO_2 from the flue gas stream with an alkali scrubbing solution having a pH greater than six, and removing any alkali aerosols generated by the scrubbing steps and oxidized mercury with an aerosol removal means. A portion of the oxidized mercury may be removed from the gas stream with the scrubbing solution. These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description, drawings, and claims.

Brief Description of Drawings

[0012] FIG. 1 is a process flow chart showing the process of the present invention.

[0013] FIG. 2 is a cut-away view of an apparatus according to the present invention.

[0014] FIG. 3 is a chart showing final NO_2 concentration from various alkalis as a function of pH.

[0015] FIG. 4 is a chart showing final SO_2 concentration from various alkalis as a function of pH.

Detailed Description

[0016] The present invention is a process and apparatus for removing SO_2 , Hg, NO, and NO_2 from a gas stream, especially from the flue gas stream of a fossil fuel boiler. In practice, flue gas from the combustion of fossil fuel nearly always contains more NO than NO_2 , and often contains Hg, which can also be removed from the gas stream by this invention.

[0017] The inventors are familiar with methods and apparatuses for removing SO_2 and NOx from gas streams. U.S. Patent Nos. 5,871,703, and 6,117,403 teach the use of an electrical discharge apparatus to oxidize SO_2 and NOx to form sulfuric and nitric acids respectively, collecting the acids in a wet electrostatic precipitator ("WESP") to form an effluent, and processing the effluent to make industrial grade acids that can be sold. It also teaches converting NO to NO_2 . The inventors on these two patents are Alix, Neister, and McLarnon, two of whom are inventors of the present invention. U.S. Patent No. 6,132,692 teaches the use of a dielectric barrier discharge ("DBD") reactor to form the same acids, collecting them in a WESP, and draining them from the WESP to remove them from a gas stream. The inventors on this patent are Alix, Neister, McLarnon, and Boyle, two of whom are inventors of the present invention. The above three patents were owned by the owner of the present invention as of the filing date of this specification. They are hereby incorporated by reference as if completely rewritten herein.

[0018] The present invention comprises a three-step process as shown in FIG. 1. A gas stream comprising SO_2 , NO, NO_2 , and perhaps Hg, are present prior to the first step 60. The first step 60 is oxidizing at least a portion of the NO in the flue gas to NO_2 with an oxidizing means. The means selected should be able to oxidize greater than about two percent of the NO to NO_2 , and is preferably in the region of about

ninety percent.

[0019] The oxidizing step should be adjusted so that the resulting mole ratio of SO_2 to NO_2 after the oxidizing step should be at least 2 to 1. The ratio is preferably four to one, but can be greater. The oxidizing means 60 can be any means known in the art, including but not limited to using an electrical discharge reactor, and injecting ClO_2 , O_3 or certain organic compounds. For example, U.S. Patent Nos. 4,029,739 and 4,035,470 teach converting NO to NO_2 by the addition of ClO_2 or O_3 into the gas stream. U.S. Patent No. 4,971,777 teaches the addition of certain organic compounds that decompose into radicals at high temperatures.

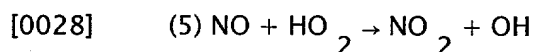
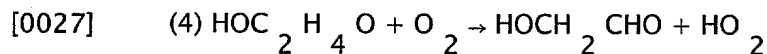
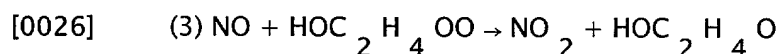
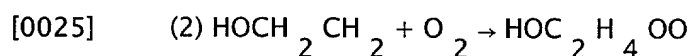
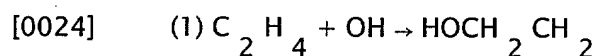
[0020] Examples of suitable electrical discharge reactors include corona, pulsed corona, e-beam, and DBD. DBD is synonymously referred to as silent discharge and non-thermal plasma discharge. It is not the same as corona discharge or pulsed corona discharge. The preferred embodiment uses a DBD reactor, such as that disclosed in U.S. Patent No. 6,132,692, by Alix, et al. In practice, the operator of the process will adjust the power input to the reactor to attain the desired oxidation results as a function of the cost of power input to the reactor, desired scrubbing results, and other factors. Laboratory testing has shown that oxidation of at least 90% of the NO and Hg is readily attainable with the present invention.

[0021] As taught in U.S. Patent No. 6,132,692, a DBD reactor will oxidize at least a portion of the NO and NO_2 in a gas stream to nitric acid, and at least a portion of the SO_2 in a gas stream to sulfuric acid. These acids are dealt with in the next step of the process.

[0022] If oxidizing means other than an electrical discharge reactor is used, Hg may or may not be oxidized to oxidized mercury or HgO. As used in this specification, the term "oxidized mercury" is intended to include any or all of the forms of oxidized mercury that are known in the art, including without limitation, HgO and Hg^{++} . On the other hand, it is possible, and perhaps desirable, that some of the NO and NO_2 becomes further oxidized to form HNO_3 regardless of the means used. The reason why this may be desirable will be made clear later in this specification.

[0023] Another way to carry out the oxidizing step 60 is adding an alkene such as ethene

or propene to the flue gas followed by oxidizing NO to NO₂ with an oxidizing means, such as the electrical discharge reactor. This would have the advantage of reducing the power input requirement of the electrical discharge reactor to get the same amount of NO to NO₂ oxidation. The alkene can be added in about a 0.3:1 molar ratio of propene to NO, or 0.5 molar ratio of ethene to NO. The likely chemical reaction mechanisms for the conversion of NO to NO₂ in the case where ethene is the alkene selected for use with an electrical discharge reactor are as follows:



[0029] In any event, the output gas stream comprises SO₂, less NO, more NO₂, perhaps HNO₃, perhaps H₂SO₄, and perhaps oxidized mercury, as shown in FIG. 1.

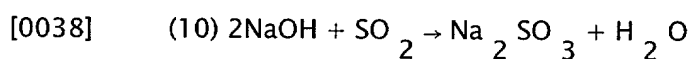
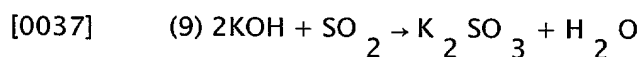
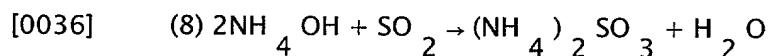
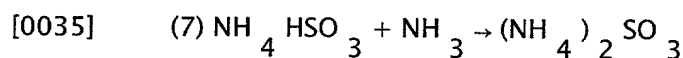
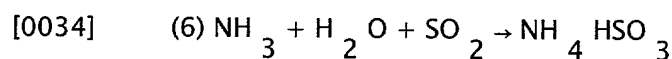
[0030] The second step 62 is scrubbing at least a portion of the SO₂, NO, and NO₂ present in the gas stream with an aqueous alkali or ammonium scrubbing solution. Some of the oxidized mercury may also be scrubbed in this step 62. For the purposes of this specification, ammonium shall be considered an alkali. The term "scrubbing" typically means "absorbing" to people having skill in the art, meaning that SO₂, NO, and NO₂ is absorbed by the aqueous solution. However, it is intended that the term "scrubbing" as used in this specification also includes adding anhydrous ammonia to the scrubbing solution to initiate the reactions leading to the oxidation of SO₂ and reduction of NO₂.

[0031] The solution preferably comprises at least one alkali, alkali sulfite, alkali sulfate, and water. The alkali can be any one that is capable of maintaining the scrubbing solution at the desired pH. Preferably, the alkalis are one or more of ammonium, sodium, and potassium. The solution preferably has a pH greater than six, which is much higher than that taught by Firnhaber. Firnhaber teaches that the pH must be

kept to less than five, and is preferably 4.5, to prevent the formation of aerosols. However, the present invention is not concerned with avoiding the formation of aerosols because it includes an aerosol removal means 64, described later in this specification.

[0032] Maintaining a relatively high pH has several benefits. It increases the speed of absorption of SO_2 . It increases the ratio of sulfite available in solution compared to bisulfite, which facilitates the oxidation of SO_2 and reduction of NO_2 . The ratio of sulfite to bisulfite is highly dependent on pH level. From these benefits, it follows that the absorption vessel, shown as item 44 in FIG. 2, can be substantially smaller than that used to scrub the same amount of SO_2 in a conventional limestone scrubber which is the most typical SO_2 scrubber in use today. In addition, the amount of scrubbing liquid required and the liquid to gas ratio can be reduced. It is estimated that the size of the absorption vessel 44 can be reduced by half, and the liquid to gas ratio can be reduced by 75%. Because the cost of the absorption vessel and liquid circulating equipment represent a large fraction of the total cost of a scrubber, the ability to substantially reduce the size of the vessel and associated pumps and piping is a major advantage of the present invention over the prior art.

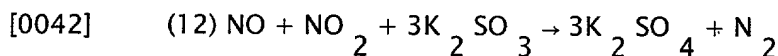
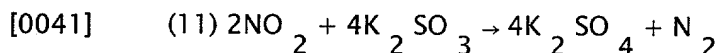
[0033] Although FIG. 1 shows alkali hydroxide being added at this step, anhydrous ammonia in the form of ammonium hydroxide can be added instead. The alkali hydroxide reacts with the gas stream output from the oxidizing step, forming alkali sulfite and alkali bisulfite. The likely chemical reactions in this step, in the case of ammonia, potassium hydroxide, and sodium hydroxide, are as follows:



[0039] An oxidation inhibitor can be added at this step to inhibit the oxidation of sulfite to sulfate before the sulfite can perform its NO_2 reduction function. Examples of

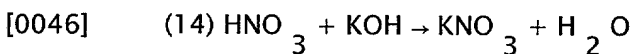
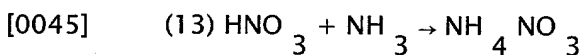
oxidation inhibitors include thiosulfate, thiourea, sulfide, and emulsified sulfur.

[0040] The alkali bisulfite and alkali sulfite react with the NO and NO₂ to form their alkali bisulfate and alkali sulfate. Ammonium sulfate and potassium sulfate, for example, are well known as valuable agricultural fertilizers. The likely reactions that take place in this step, in the case where potassium is the alkali, are as follows:



[0043] There are corresponding reactions for the case when ammonium and/or sodium are used as the alkali.

[0044] Most of the HNO₃ that may have been formed by further oxidation of NO and NO₂, and/or created by a DBD reactor, will react with the alkali and form its alkali nitrate. Potassium nitrate and ammonium nitrate are also known to be valuable agricultural fertilizers, and are formed according to the following formulae:



[0047] If another alkali is used, it will react with the nitric acid to form alkali nitrate. In a similar way, most of the sulfuric acid created by the DBD reactor will react with the solution and form alkali bisulfate, which can be further reacted to form an alkali sulfate. As one can see from the above equations, the process removes SO₂, NO, and NO₂ from the gas stream, and produces alkali nitrate, alkali sulfate, and nitrogen. Over time, the alkali sulfate and alkali nitrate will concentrate in the aqueous alkali scrubbing solution and precipitate out of solution. The solid precipitate can then be removed from the scrubber and processed for use as fertilizer, or land filled.

[0048] The gas stream after the scrubbing step comprises nitrogen and water. Since the pH of the scrubbing solution is higher than about five, the output from the scrubbing step will likely contain aerosols and ammonia vapor if ammonia was used. If not collected in the scrubbing solution, the gas stream will also contain oxidized mercury.

[0049] The third step 64 is removing at least a portion of the aerosols and the remainder

of the oxidized mercury, if present, from the gas stream. A wet electrostatic precipitator ("WESP") and/or mist eliminator may be used as the aerosol removal means. A WESP is effective at collecting alkali aerosols, oxidized mercury, and any other aerosols or particles that may be present in the gas stream.

[0050] As a result of this three-step process, SO_2 , NO, NO_2 , and Hg are removed from a gas stream to provide alkali sulfate and alkali nitrate. The output of the aerosol removal means comprises N_2 as a result of the process of the present invention.

[0051] An apparatus according to the present invention is shown in FIG. 2. A gas stream 14 comprising SO_2 , NO, NO_2 , and perhaps Hg enters the apparatus assisted by a forced draft fan 12. The gas then enters a means for oxidizing 10 at least a portion of the NO in the gas stream to NO_2 . The oxidation means 10 performs the oxidizing step 60 shown in FIG. 1, which is more fully described above. In the preferred embodiment, at least one DBD reactor is used as an oxidizing means, and can be provided in modules 16 to facilitate manufacture and installation. At least one power supply and controller is required to operate a DBD reactor, which are selected by those having skill in the art, but are not shown in the drawings.

[0052] After the oxidation means 10, the gas stream 18 comprises less SO_2 , less NO, more NO_2 , perhaps HNO_3 , perhaps H_2SO_4 and perhaps oxidized mercury. The gas stream temperature at this point is about 175°C (350°F). The gas stream then enters a scrubbing vessel 44 into a region 19 over an aqueous alkali sulfate solution 22. Preferably, the aqueous alkali sulfate solution comprises the alkali, alkali sulfite, alkali sulfate, and water. Some of the water in the alkali sulfate solution 22 evaporates due to the heat of the incoming gas stream 18, thus concentrating the solution. A portion of the solution 22 is pumped by a circulation pump 50 to a filtration / granulation apparatus 54, which is shown in FIG. 2 as a black box. The apparatus 54 actually comprises many parts, and is readily designed by persons having ordinary skill in the art. The output of the filtration / granulation apparatus 54 is a solid alkali sulfate / nitrate product 56, which can be sold as an agricultural fertilizer, depending on the alkali used.

[0053] Air 17 is introduced into the alkali sulfate solution 22 for oxidizing alkali sulfite into alkali sulfate. Alkali sulfate solution 22 is pumped with a circulation pump 50 also

to a set of lower spray nozzles 24 that serve to cool and saturate the gas stream 18 with the aqueous solution. Some of the solution is also pumped by circulation pump 50 to the WESP spray header 42 to wet the WESP 40 electrode surfaces.

[0054] Another circulation loop is provided wherein aqueous alkali sulfite and sulfate in a vessel 48 is pumped with a circulation pump 52 to a set of upper spray nozzles 34. The liquid then falls to a dual flow tray 30. A separator tray 26 allows some of the liquid to fall into the alkali sulfate solution 22, and the remainder is piped to the vessel 48. Makeup water 20 is added directly to the vessel 48. Makeup alkali 32 is added to the upper spray nozzles 34. These two circulation loops, independently or together, perform the scrubbing step 62 of FIG. 1, which is described in detail above.

[0055] Following the scrubbing loops, a WESP 40 is provided to remove any oxidized mercury leaving the scrubbing loop and alkali aerosols that may have formed earlier in the process. The WESP 40 is preferably a shell-and-tube type of WESP, but can be a plate type, or any WESP such as is known by those having skill in the art. The WESP 40 is wetted using a set of sprays 42 fed from the scrubbing solution 22 and circulation pump 50. A bubble cap tray 38 can be provided below the WESP 40. A portion of the liquid in the bubble cap tray 38 may be diverted directly to the scrubbing solution section 22 before falling through the scrubbing loops. The WESP 40 is an example of the aerosol removal means 64 described in FIG. 1, which can also be a mist eliminator alone or a combination of mist eliminators and WESPs. The gas stream exiting the WESP 40 has considerably less NO_x and SO₂ than that which entered the process and apparatus, and has an increased amount of the reaction products, which are nitrogen and water.

[0056] The following laboratory-scale examples of the process demonstrate the efficacy of the present invention:

[0057] EXAMPLE 1

[0058] An absorption test was done for the scrubbing step of the process of the present invention, with a solution that was 1% w/w SO₃²⁻ ("sulfite"), 6% w/w SO₄²⁻ ("sulfate"), and 2.5% S₂O₃²⁻ ("thiosulfate") in a packed column that was 46 cm (18 inches) high and 3.8 cm (1.5 inches) in diameter. The column was packed with 6.35

mm (0.25 inch) glass RASCHIG rings. The simulated flue gas at the inlet of the column contained 13% v/v moisture, 6% v/v O₂ and the simulated flue gas pollutants listed in Table 1. There was continuous addition of NH₃ and (NH₄)₂S₂O₃ to maintain a pH of 6.8 and a thiosulfate concentration of 2.5% w/w. The residence time in the column was 1.8 sec with an L/G ratio of 25 gpm/kacfm.

[0059] Table 1 shows the concentrations of NO, NO₂, and SO₂ at the inlet and outlet of the test system.

[0060]

[t1]

[Table 1: Scrubbing Step Alone]

	System Inlet	System Outlet
NO (ppmv)	20	4
NO ₂ (ppmv)	250	36
SO ₂ (ppmv)	1370	2

[0061] EXAMPLE 2

[0062] An absorption test was done to determine steady state operating conditions for a system with inlet flue gas conditions of 7 ppmv NO, 248 ppmv NO₂, 1485 ppmv SO₂, 6% v/v O₂ and balance N₂. NaOH and NaS₂O₃ were added to the solution to maintain a pH of 8.0 and thiosulfate concentration of 1%. The concentrations of sulfite and sulfate in the system were allowed to build to steady state. The NO_x removal rate was 77% at concentrations of SO₃²⁻, SO₄²⁻, and S₂O₃²⁻ of 1.25% w/w, 9.5% w/w, and 1.0% w/w respectively.

[0063] EXAMPLE 3

[0064] Tests were conducted in a laboratory test facility for the NO oxidizing, scrubbing, and aerosol removal steps of the process of the present invention. The equipment consisted of a simulated flue gas delivery system, a coaxial cylinder DBD reactor, a packed column scrubber and a tubular WESP. The following is an example of data

obtained in the lab test facility.

[0065] Simulated flue gas was delivered to the DBD reactor at a flow rate of 0.4 m³/minute (14 scfm), a temperature of 143 °C (290 °F) and with the following composition: 6.2% v/v O₂, 14.2% v/v CO₂, 8.2% v/v H₂O, 20 ppmv CO, 250 ppmv C₂H₄, 1740 ppmv SO₂, and 259 ppmv NO_x. Gas velocity through the discharge reactor was 15.2 m/s (50 ft/s) with a discharge power level of 140 watts. Gas from the discharge reactor entered a 10.2 cm (4 inch) ID packed column scrubber, packed with 1.3 cm (0.5 inch) INTALOX saddles to a depth of 1.2 m (4 ft.). Liquid was introduced at the top of the scrubber at a flow rate of 1.25 liters/minute (0.33 gpm) (L/G= 20 gpm/kacfm). Aqueous ammonia was added to and effluent liquid removed from the recirculating scrubber solution to maintain a constant total liquid volume and solution pH at 6.6. Gas from the packed bed scrubber was treated in a 10.2 cm (4 inch) ID wetted wall electrostatic precipitator with a gas residence time of 0.7 seconds.

[0066] Table 2 below shows the concentrations of NO, NO₂ and SO₂ at the inlet to the system, the outlet of the barrier discharge reactor and at the outlet of the system.

[0067]
[t2]

[Table 2: Three Step Process]

	System Inlet	Discharge Reactor Outlet	System Outlet
NO (ppmv)	254	45	32
NO ₂ (ppmv)	5	109	9
SO ₂ (ppmv)	1740	1598	1

[0068] FIG. 3 is a chart showing actual experimental data of final NO₂ concentrations in a process according to the present invention as a function of pH. The results using sodium, ammonium, and potassium are shown as different data sets. The initial conditions were a temperature of 54 °C (130 °F), 0.5% SO₃²⁻ concentration, and initial SO₂ concentration of 1500 ppm. FIG. 4 is a chart showing actual experimental data of final SO₂ concentrations in a process according to the present invention as a

function of pH. The results using sodium, ammonium, and potassium are shown as different data sets. The initial conditions were a temperature of 54 ° C (130 ° F), 0.5% SO_3^{2-} concentration, and initial NO_2 concentration of 250 ppm.

[0069] The three-step process and apparatus described herein was designed specifically to treat flue gas from a coal fired power plant. However, it can be appreciated that the invention is capable of operating on any gas stream in which NO_x and SO_2 are present, including but not limited to gas and oil-fired boilers and various chemical manufacturing processes. The NO_x and SO_2 concentrations and operating conditions will be different in each situation. Therefore, it is understood that an operator or system designer will be motivated to modify the scrubbing step 62 to possibly eliminate the need for either one or both the oxidizing step 60 or the aerosol removal step 64, or combine the three elements somehow so that fewer than three steps are needed.

[0070] It will be apparent to those skilled in the art that various changes and modifications can be made without departing from the spirit of the present invention. Accordingly, it is intended to encompass within the appended claims all such changes and modifications that fall within the scope of the present invention.

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